tained from eq. 5 was corrected to give the value shown in Table IV.

The apparatus and methods of infrared analysis and of calculation of the extent of deuteration of deuterated haloforms have been described previously.[12] The following extinction coefficients were used in the present work. For $CHFI_2$, $\epsilon_{9.173}$ 428.4 ± 0.6, $\epsilon_{9.475}$ 171 ± 0.4, $\epsilon_{9.622}$ 70.4 ± 0.8, $\epsilon_{9.752}$ 272.9 ± 1.6, $\epsilon_{12.154}$ 0.00 ± 0.2; $CDFI_2$, $\epsilon_{9.173}$ 200.2 ± 0.4, $\epsilon_{9.475}$ 110.8 ± 2.5, $\epsilon_{9.622}$ 260 ± 3.1, $\epsilon_{9.752}$ 157 ± 1.2, $\epsilon_{12.154}$ 308.4 ± 3.1; $CHBr_2F$, $\epsilon_{11.226}$ 324.5 ± 2.5, $\epsilon_{14.204}$ 0.00 ± 0.2; $CDBr_2F$, $\epsilon_{11.226}$ 0.00 ± 0.2, $\epsilon_{14.204}$ = 597 ± 8.

Acknowledgment.—The authors wish to thank Dr. Stanton J. Ehrenson for checking many of the calculations and derivations carried out during this investigation.

ATLANTA, GEORGIA

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE GEORGIA INSTITUTE OF TECHNOLOGY]

The Effect of Structure on the Relative Stability of Dihalomethylenes[1]

BY JACK HINE AND STANTON J. EHRENSON

RECEIVED AUGUST 26, 1957

The relative reactivities of ten haloforms toward hydrolysis in aqueous solution are correlated in terms of an equation based on the dihalomethylene reaction mechanism. This equation uses the known carbanion formation rate constants and contains parameters for (1) the relative abilities of the various halogens to stabilize dihalomethylenes, (2) the relative ease with which halogens are separated as anions from the intermediate trihalomethyl anion, and (3) the carbanion character of the transition state for dihalomethylene formation. From the values of these parameters, halogens appear to facilitate dihalomethylene formation in the order F ≫ Cl > Br > I. Since the dihalomethylenes appear to be non-radicals rather than diradicals, this order is attributed to the relative abilities of the halogens to supply electrons to the carbon atom by tautomeric effects. The relative electrophilic and nucleophilic characters of several methylenes are discussed in terms of these parameters. The parameters for the differences between the abilities of halogens to separate as anions (Br > I > Cl) are smaller and probably less significant. The transition state for dihalomethylene formation appears to have considerable carbanion character. For the basic decomposition reactions in methanol and aqueous dioxane, where carbanion formation rates are not known, equations are developed for correlating the data on smaller groups of haloforms. When an inhibitor is used to prevent the free radical reactions that occur with certain haloforms in these solvents, the rate constants obtained fit the equations satisfactorily.

Introduction

In earlier articles of this series evidence was presented that at least some haloforms undergo alkaline hydrolysis by the mechanism

$$CHX_3 + OH^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CX_3^- + H_2O \qquad (I)$$

$$CX_3^- \xrightarrow{k_2} CX_2 + X^-$$

followed by rapid reactions of CX_2. Some of the first evidence that haloforms hydrolyze by this mechanism was the fact that their reactivities are so much greater than would be expected from the S_N2 mechanism.[2] Since mechanism I explains the great reactivity of haloforms in general, toward basic hydrolysis, we hoped to be able to use this mechanism in correlating the relative reactivities of different haloforms, thus learning more about the ease of formation and hence perhaps the relative stabilities of various dihalomethylenes. We obtained data on the relative reactivities of six haloforms in 66²/₃% dioxane–water solution,[3] which would have sufficed for a *qualitative* discussion of the effect of structure on reactivity, but by this time it was beginning to appear that the relative reactivities might be correlated *quantitatively* if values of k_1, the rate constant for the initial carbanion formation, were available. Unfortunately, these values were not available and, in fact, would be rather difficult to determine in such a solvent.[4] However, the kinetics of carbanion formation from haloforms may be studied by deuterium exchange experiments in purely aqueous solution, and data on a number of haloforms have been obtained in this solvent.[5–8] We therefore have determined rate constants for the basic hydrolysis of a number of haloforms in aqueous solution and correlated these rate constants in terms of the values of k_1 and of certain additional parameters by use of an equation based on mechanism I.

Discussion and Results

The Correlation Equation.—In terms of the rate constants for the individual steps of the reaction, the over-all rate constant for hydrolysis may be expressed

$$k_h = \frac{k_1(k_2/k_{-1})}{1 + (k_2/k_{-1})}$$

Since the values of k_1 are known (or may be closely approximated by estimating the kinetic isotope effect), a correlation of the values of k_2/k_{-1} is equivalent to a correlation of k_h values. The fraction k_2/k_{-1} is simply the rate constant by which the trihalomethyl anion yields dihalomethylene divided by the rate constant for its abstraction of a proton from water to re-form haloform.

The generality of applicability of the Brönsted catalysis law shows that the acids that donate pro-

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(1) Part XI in the series "Methylene Derivatives as Intermediates in Polar Reactions." For part X see preceding paper. This work was supported in part by the Office of Ordnance Research, U. S. Army, and was presented in preliminary form at the Sixth Biannual Conference on Reaction Mechanisms, Swarthmore, Pa., Sept. 13, 1956.

(2) J. Hine, THIS JOURNAL, **72**, 2438 (1950).

(3) J. Hine, A. M. Dowell, Jr., and J. E. Singley, Jr., *ibid.*, **78**, 479 (1956).

(4) The dioxane would be extracted, with the haloform, in the first step of the isotopic analysis in the required deuterium exchange experiments.

(5) J. Hine, R. C. Peek, Jr., and B. D. Oakes, THIS JOURNAL, **76**, 827 (1954).

(6) J. Hine and N. W. Burske, *ibid.*, **78**, 3337 (1956).

(7) J. Hine, N. W. Burske, M. Hine and P. B. Langford, *ibid.*, **79**, 1406 (1957).

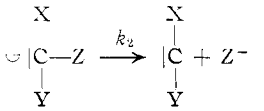
(8) J. Hine, R. Butterworth and P. B. Langford, *ibid.*, **80**, 819 (1958).

tons most rapidly are usually those whose conjugate bases accept protons the slowest. While the number of exceptions to this generalization is considerable,[9] we shall assume that it holds for the haloforms, particularly since they form a series of closely related compounds and their acid-base reactions should not be complicated by such things as internal rotation and steric inhibition of resonance. Putting this generalization in a quantitative form and using chloroform as a reference compound

$$\log \frac{k_{-1}^{\mathrm{CHXYZ}}}{k_{-1}^{\mathrm{CHCl_3}}} = -c \log \frac{k_1^{\mathrm{CHXYZ}}}{k_1^{\mathrm{CHCl_3}}} \qquad (1)$$

where c is a dimensionless proportionality constant that may be thought of as the amount of change in carbanion character between the trihalomethyl anion and the transition state for its protonation divided by the change in carbanion character between the haloform and the transition state for carbanion formation.

We assume that three factors control the relative values of k_2.



$$\smile|\underset{\mathrm{Y}}{\overset{\mathrm{X}}{\mathrm{C}}}\text{—}\mathrm{Z} \xrightarrow{k_2} |\underset{\mathrm{Y}}{\overset{\mathrm{X}}{\mathrm{C}}} + \mathrm{Z}^-$$

One factor relates to the ease with which the halogen (Z in the equation above) that is departing as an anion in the transition state breaks away from carbon with its bonding electron pair. The second factor relates to the ability of the two halogen atoms (X and Y above) that remain attached to carbon to stabilize the dihalomethylene that is being formed in the transition state. The existence of the third factor depends on the fact that the carbanion character of the reactant is decreasing in the transition state. Therefore whatever tends to stabilize a carbanion will lower k_2. Assuming that the factors that control carbanion stabilization are adequately measured by k_1 and that the effects of changes in various factors on the free energy of activation will be linear, we arrive at the following equation in which the reactivity is expressed relative to chloroform as a standard.

$$\log \frac{k_2^{\mathrm{CHXYZ}}}{k_2^{\mathrm{CHCl_3}}} = M_{\mathrm{X}} + M_{\mathrm{Y}} + N_{\mathrm{Z}} + \log \frac{n_{\mathrm{Z}}}{3} - d \log \frac{k_1^{\mathrm{CHXYZ}}}{k_1^{\mathrm{CHCl_3}}} \qquad (2)$$

M_{X} and M_{Y} are the methylene stabilization factors for the two halogens that become a part of the dihalomethylene; N_{Z} is a constant for that halogen being lost as an anion in the transition state; $\log (n_{\mathrm{Z}}/3)$ is a statistical factor in which n_{Z} is the number of halogens of the type being lost and the "3" refers to the fact that there are 3 of these in chloroform; and d is a dimensionless proportionality constant (assumed, like c, to be the same for all haloforms) for the trihalomethyl anion, being equal to the amount of carbanion character it has lost in the transition state for protonation divided by that lost in the transition state for dihalomethylene formation. Our use of chloroform as the reference compound defines M_{Cl} and N_{Cl} as zero.

Combining equations 1 and 2 we obtain

$$\log \frac{(k_2/k_{-1})_{\mathrm{CHXYZ}}}{(k_2/k_{-1})_{\mathrm{CHCl_3}}} = M_{\mathrm{X}} + M_{\mathrm{Y}} + N_{\mathrm{Z}} + \log \frac{n_{\mathrm{Z}}}{3} + (c - d) \log \frac{k_1^{\mathrm{CHXYZ}}}{k_1^{\mathrm{CHCl_3}}} \qquad (3)$$

This equation, of course, predicts only that part of the haloform hydrolysis rate that is due to the loss of halogen anions of the type of Z. While it should be used in the form shown for symmetrical haloforms (in which X = Y = Z), with "mixed" haloforms the total reaction rate is equal to the sum of the rates for reaction *via* loss of halogens of each of the kinds present.

Correlation in Aqueous Solution.—In order to test equation 3, rate constants were determined for the hydrolysis of a number of haloforms in aqueous solution at several temperatures. Determinations were made for all of the compounds for which deuterium exchange data are available except for iodoform, whose low solubility, low reactivity and great sensitivity to air and light made such measurements inconvenient. The resultant data are listed in Table I. All of the haloforms studied appear to hydrolyze by the dihalomethylene mechanism. Rate retardation by added halide ions ("mass-law effect") has been observed for chloroform,[2] bromodichloromethane[8] and dibromochloromethane.[8] The reaction of these three haloforms and of bromoform with sodium *p*-thiocresolate has been found to be catalyzed by base.[3] All of the compounds are known to undergo base-catalyzed deuterium exchange and to hydrolyze much more rapidly than would be expected, by extrapolation from data on methyl[10,11] and methylene halides,[3,11] by the S$_N$2 mechanism.[12]

For seven of the haloforms, we had available only the rate constants for carbanion formation from the deuteriohaloforms. From these we calculated k_1's, the values for the protium compounds, by use of deuterium kinetic isotope effects of 1.75 at 0° and 1.43 at 50°, these values being the average of those found at 0° and extrapolated to 50° for dichlorofluoromethane[6] and bromochlorofluoromethane,[7] the two haloforms for which kinetic isotope effects have been determined. The k_1 values for chlorodiiodomethane were assumed to be the same as those for chlorodibromomethane since the values for bromoform and iodoform are essentially equal as are those for dichloroiodomethane and bromodichloromethane at 0°. Because of this latter near-equality at 0°, k_1 for bromodichloromethane at 50° was assumed to be equal to k_1 for dichloroiodomethane at 50°. Rate constants were extrapolated to 0 and 50° when necessary by use of plots of $\log k$ *vs.* $1/T$.

Optimum values of the parameters of eq. 3, calculated by the method of least squares, are listed in Table II. The values of $\log (k_2/k_{-1})$ at 0° calculated from these parameters are listed in Table

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[9] *Cf.* R. G. Pearson and R. L. Dillon, THIS JOURNAL, **75**, 2439 (1953).

[10] E. A. Moelwyn-Hughes, *Proc. Roy. Soc.* (*London*), **A196**, 540 (1949).

[11] J. Hine, C. H. Thomas and S. J. Ehrenson, THIS JOURNAL, **77**, 3886 (1955); J. Hine, S. J. Ehrenson and W. H. Brader, Jr., *ibid.*, **78**, 2282 (1956).

[12] For the significance of the terms S$_N$2 and S$_N$1 see J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., Chap. 5.

TABLE I

KINETIC CONSTANTS FOR THE BASIC HYDROLYSIS OF HALOFORMS IN AQUEOUS SOLUTION

Compound	$10^4 k_b$ l. mole^{-1} sec.$^{-1}$ 0.0°	20.0°	35.0°	50.0°	$\Delta H^\ddagger$, kcal./mole	$\Delta S^\ddagger$, e.u.
$CHClI_2$	0.0010[a]		112 ± 25[b,c]	9.2 ± 0.3	31.3 ± 3.0	24.2 ± 10
$CHCl_3$	.0060 ± 0.0004	0.23 ± 0.01	2.41 ± 0.03	18.8 ± 0.6	27.7 ± 0.5	14.4 ± 2
$CHBr_3$	.0240[a]	1.99 ± .03[d]	9.54 ± .14	84 ± 3[c]	28.1 ± .3	18.6 ± 1
$CHCl_2I$	.0260[a]	2.17 ± .03[d]	11.6 ± .8[c]	95 ± 6[c]	28.3 ± .5	19.7 ± 2
$CHBr_2Cl$	.0665 ± 0.002[e]		56 ± 2[e,f]	220 ± 13[e]	27.9 ± .5	19.9 ± 2
$CHCl_2F$[g]	.123 ± .001	3.95 ± 0.04[h]		300[m]	26.8 ± .3	17.2 ± 1
$CHBrCl_2$	.149 ± .002[e]	102 ± 2[e,f]	49 ± 3	354 ± 8	27.1 ± .5	18.9 ± 2
$CHFI_2$[e]	1.53 ± .03	61.5 ± 1.3[i]		4900[m]	27.8 ± .5	25.9 ± 3
$CHBrClF$[j]	13.2 ± .2	150 ± 5[k]		18000[m]	24.8 ± .5	19.2 ± 2
$CHBr_2F$[e]	27.7 ± .3	708 ± 30[l]		50000[m]	25.7 ± .5	24.1 ± 2

[a] Extrapolated from data at higher temperatures. [b] At 67.1°. [c] Rate constant determined graphically. [d] At 25.0°. [e] Data from ref. 8. [f] At 40°. [g] Data from ref. 6. [h] At 20.2°. [i] At 20.85°. [j] Data from ref. 7. [k] At 15.0°. [l] At 19.6°. [m] Extrapolated from data at lower temperatures.

TABLE II

VALUES OF THE PARAMETERS OF EQUATION 3

	0°	50°		0°	50°
M_F	3.727	3.193	N_{Br}	0.785	0.936
M_{Br}	−1.461	−1.131	N_I	.118	.486
M_I	−2.626	−2.039	$(c - d)$	.299	.196

III with the values calculated from the experimental data. The average deviation, 0.027, corresponds to a 6% average error in the haloform hydrolysis rate constants that may be calculated from eq. 3. This is no larger than the probable error in the experimental determination of k_2/k_{-1}. At 50°, where more of the rate constants (including all of those for carbanion formation) were calculated by extrapolation, the average deviation was 0.053 or 13% in the rate constants.

TABLE III

COMPARISON OF EXPERIMENTAL VALUES OF LOG (k_2/k_{-1}) WITH THOSE CALCULATED FROM EQUATION 3 AT 0°

Haloform	$-\log (k_2/k_{-1})$[a] Exptl.	Eq. 3	Haloform	$-\log (k_2/k_{-1})$[a] Exptl.	Eq. 3
$CHClI_2$	6.400	6.377	$CHBrCl_2$	3.532	3.593
$CHBr_3$	5.626	5.649	$CHFI_2$	2.763	2.785
$CHCl_2I$	4.267	4.267	$CHBrClF$	0.246	0.208
$CHBr_2Cl$	4.577	4.545	$CHBr_2F$	1.082	1.069
$CHCl_2F$	1.071	1.100			

[a] Based on the value 4.137 for chloroform.

The use of as many as six parameters to correlate nine values of log (k_2/k_{-1}) may seem to detract from the argument that the observed agreement with eq. 3 supports the proposed reaction mechanism. It is our feeling, however, that the evidence for the reaction mechanism is already adequate, and that since the three factors corresponding to the M, N and c-d parameters are certainly those that should logically be related to reactivity by this mechanism, these factors are best measured by some quantitative correlation such as eq. 3.

The correlation was made on the assumption that in a haloform containing both chlorine and bromine or chlorine and iodine, the reaction involves almost entirely the loss of bromide or iodide ion in the rate-controlling step, with chloride ion loss being only a negligible side reaction. The values of the parameters obtained justify this assumption. From eq. 3 it follows that if k_2^{Cl} is the rate constant for the rate-controlling loss of chloride ion from the mixed haloform, CHX_nCl_{3-n}, and k_2^X is the rate constant for the loss of the other halide, then

$$\log \frac{k_2^X}{k_2^{Cl}} = N_X - M_X + \log \frac{n}{3 - n} \qquad (4)$$

Calculations using eq. 4 show that in none of the bromine- or iodine-containing haloforms studied should the rate-controlling loss of chloride ion comprise more than 2% of the total reaction. It also seems very unlikely that the loss of fluoride ion is a significant part of any reaction. Our consideration of only one reaction path for each of our haloforms is therefore justified. With haloforms containing both bromine and iodine, however, the loss of each may contribute significantly to the reaction as a whole.

Interpretation of the Parameter Values.—The largest of the parameters of eq. 3 are the M-values. The M_F and M_I values (at 0°) show that the replacement of one iodine atom of a trihalomethyl anion by a fluorine lowers the activation energy for dihalomethylene formation by 8 kcal./mole, corresponding to an effect on k_2/k_{-1} of more than two-million fold. Our interpretation of these M-values, however, must depend on whether the dihalomethylenes being formed are in the singlet (non-radical) or triplet (diradical) state. From the magnitudes of the bathochromic shifts in the ultraviolet spectra of alkyl iodides that are produced by various substituents, it appears that α-halogens have the following relative abilities to stabilize free radicals: I > Br > Cl > F.[13] This conclusion is supported by determinations of the bond dissociation energies of various aliphatic iodides[14] and bromides[15] and to some extent by data on the relative reactivities of halomethanes toward sodium in the vapor phase.[16] Thus if triplet dihalomethylenes were being formed we might have expected the order $M_I > M_{Br} > M_{Cl} > M_F$. On the other hand if a singlet is being formed the process is simply an SN1 reaction[12] of a carbanion, and

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(13) R. N. Haszeldine, *J. Chem. Soc.*, 1764 (1953).

(14) E. T. Butler, E. Mandel and M. Polanyi, *Trans. Faraday Soc.*, **41**, 298 (1945); F. P. Lossing, K. U. Ingold and I. H. S. Henderson, *J. Chem. Phys.*, **22**, 1489 (1954).

(15) M. Szwarc and A. H. Sehon, *ibid.*, **19**, 656 (1951).

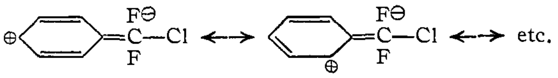
(16) E. W. R. Steacie, "Atomic and Free Radical Reactions," 2nd Ed., Reinhold Publishing Corp., New York, N. Y., 1954, chap. XIII.

α-halogen substituents might be expected to have the same effect that they do in other SN1 reactions. However, in the only case that appears to have been studied, α-halogens facilitated SN1 reactivity in the order Cl > Br > F.[17]

Since neither the radical nor non-radical mechanism permits a satisfactory *prediction* of our *M*-values from reactivity data in reactions of known mechanism, we must distinguish between these possibilities on the basis of other evidence. The singlet structure for dihalomethylenes, in which the carbon atom is left with a vacant orbital, is in agreement with the considerable evidence that these species behave as electrophilic reagents. Thus, for example, there is a linear relationship between the nucleophilicities of halide ions and their relative reactivities toward dichloromethylene that extends even to the amphoteric reagent water.[18] Analogously Skell and Garner have found that the reactivities of olefins toward dibromomethylene are increased by electron-donating substituents.[19] The facts that the relative reactivities of olefins toward dibromomethylene do *not* parallel their reactivities toward halomethyl radicals[19] and that the additions of dibromomethylene and even methylene itself to olefins are stereospecifically *cis*[20] provide even more evidence for the non-radical nature of dihalomethylenes.

Another strong argument that dihalomethylenes have a singlet (and non-linear) structure is based on theoretical and spectroscopic considerations. Walsh has reviewed and re-emphasized the evidence that the geometry of molecules of the B–A–C type is determined by the number of valency electrons.[21] Each of the seven species having eighteen valency electrons upon which he quotes structural data has a bond angle in the range 120 ± 10° and each is a singlet. These include the species NOCl and NOBr, which are isoelectronic with our intermediates, CFCl and CFBr. Even more directly relevant are the data on CF_2, a dihalomethylene, although not an intermediate in any of the hydrolyses studied herein. The spectrum of this molecule offers evidence for a non-linear singlet structure.[21,22] With the dihalomethylenes derived from the higher halogens, the triplet state should be lower-lying with respect to the singlet than is the case with CF_2, and it is possible the triplet is the more stable form in CI_2. Nevertheless we shall assume that the trihalomethyl anions lose halide ions to give dihalomethylenes without concomitant change in multiplicity.

On this basis we attribute the observed order, $M_F >> M_{Cl} > M_{Br} > M_I$, to the relative abilities of the four halogens to supply electrons to the deficient carbon atom. This sequence agrees with Taft's recent quantitative evaluation of the relative ability of the halogens to supply electrons by resonance[23] as well as with earlier qualitative assessments of the positive electromeric and mesomeric effects.[24] The observed greater reactivity of $C_6H_5CCl_3$ compared to $C_6H_5CF_2Cl$, upon which was based the conclusion that α-chlorine facilitates SN1 reactivity better than α-fluorine,[17] may be due to several factors that do not influence the SN1 reactivity of trihalomethyl anions. For example, the benzodifluorochloride must be stabilized by the contribution of such resonance structures as[25]



This resonance, which has no analog in the trihalomethyl anion, would be lost during carbonium ion formation.

Since the relative ability to stabilize carbanions appears, from the deuterium exchange data, to stand in the order Br > Cl > F, while the ability to stabilize the electron deficiency of methylenic carbon atoms appears, from the *M*-values, to vary in the order F > Cl > Br, it might be expected that the relative electrophilic character of dihalomethylenes would vary in the order $CBr_2 > CCl_2 > CF_2$, with the relative order of nucleophilicity varying in the opposite order. Recent studies on the mechanism of the basic hydrolysis of chlorodifluoromethane and bromodifluoromethane give more direct evidence for this point of view. From their reactivities as well as a deuterium-exchange study it appears that the basic hydrolysis of these two haloforms, is a concerted process in which the bromide or chloride ion is lost *as* the hydrogen atom is removed, difluoromethylene being formed in a single step not involving a carbanion intermediate.[26] From the principle of microscopic reversibility it follows that difluoromethylene, in combining with a chloride or bromide ion,[27] simultaneously accepts a proton from water. That is, in its reaction with chloride and bromide ions in aqueous solution difluoromethylene simultaneously displays both electrophilic and nucleophilic character, in contrast to dichloromethylene which acts purely as an electrophilic reagent, combining with nucleophilic halide ions to give trihalomethyl anions that are protonated only subsequently. With the recently reported alkoxyfluoromethylene intermediates[28] even more nucleophilic and less electrophilic character would be expected. In fact, it would not be surprising if these intermediates reacted with hydroxylic solvents by proton abstraction to give $ROCHF^+$ type carbonium ions.

The *N* parameters, relating to the ease of separation of the halogens as anions, correspond to bromine reacting 6–8 and iodine 1.3–3 times as fast as chlorine. While the reactivity series Br > I > Cl is not the one most commonly observed

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[17] J. Hine and D. E. Lee, THIS JOURNAL, **73**, 22 (1951); **74**, 3182 (1952).

[18] J. Hine and A. M. Dowell, Jr., *ibid.*, **76**, 2688 (1954).

[19] P. S. Skell and A. Y. Garner, *ibid.*, **78**, 5430 (1956).

[20] P. S. Skell and A. Y. Garner, *ibid.*, **78**, 3409 (1956); P. S. Skell and R. C. Woodworth, *ibid.*, **78**, 4496 (1956); W. von E. Doering and P. LaFlamme, *ibid.*, **78**, 5447 (1956).

[21] A. D. Walsh, *J. Chem. Soc.*, 2266 (1953).

[22] P. Venkateswarlu, *Phys. Rev.*, **77**, 676 (1950); R. K. Laird, E. B. Andrews and R. F. Barrow, *Trans. Faraday Soc.*, **46**, 803 (1950).

[23] R. W. Taft, Jr., THIS JOURNAL, **79**, 1045 (1957).

[24] C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, pp. 75, 89.

[25] *Cf.* J. D. Roberts, R. L. Webb and E. A. McElhill, THIS JOURNAL, **72**, 408 (1950).

[26] J. Hine and P. B. Langford, *ibid.*, **79**, 5497 (1957).

[27] D. C. Duffey has obtained evidence for the occurrence of these reactions in this Laboratory.

[28] J. Hine and K. Tanabe, THIS JOURNAL, **79**, 2654 (1957); J. Hine and J. J. Porter, *ibid.*, **79**, 5493 (1957).

in nucleophilic displacement reactions of saturated aliphatic halides, it has been reported on more than one occasion.[10,11] Even after allowing for errors in determination (parameter values differing from those listed by about 0.2 can be obtained without more than doubling the average deviation of calculated from experimental k_2/k_{-1} values) our *N*-values seem rather small, since an incomplete literature survey[11,17,29] that located more than sixty ratios of the reactivity of bromides or iodides to that of chlorides revealed $k^{\mathrm{RBr}}/k^{\mathrm{RCl}}$ values ranging from 11[29a] to 1520[29b] and $k^{\mathrm{RI}}/k^{\mathrm{RCl}}$ values ranging from 4[29a,c] to 735.[29d] It may be that for some reason, perhaps related to the carbanionic character of the reactant, the relative reactivities of bromides and iodides are smaller than usual in the present case. It is equally probable though that some of the assumptions (*e.g.*, that the transition state has the same amount of carbanion character for each haloform) that are implicit in eq. 3 are incorrect, and that for this reason our parameters may contain other factors in addition to those they were designed to measure. It therefore seems best not to attach too much significance to such small differences as those between our *N*-values.

The fact that *c* is larger than *d* ($c - d$ is positive) suggests that the trihalomethyl anions have lost more carbanion character in the transition state for their transformation to haloform than they have in the transition state leading to dihalomethylene. This is perhaps not surprising, particularly in view of the fact that considerable carbanion character still remains in the dihalomethylene (assuming a singlet state). The values of the parameters obtained are not precise enough to show with any certainty the relative extents to which they reflect entropy and enthalpy effects. It is worthwhile to point out, though, that parameters due solely to enthalpy effects should decrease in absolute value by 18% (323/273 = 1.18) between 0 and 50°, as our *M*-values tend to do, while entropy factors should remain constant.

Correlation in Methanol and Dioxane–Water.—A comparison of the data of Table I with the rate constants for hydrolysis in 66²/₃% dioxane–water already published[3] shows that the change in solvent has a variable effect on the reaction rates. Thus while chloroform hydrolyzes at about the same rate in the two solvents, dichloroiodomethane hydrolyzes more than three times and bromochlorofluoromethane more than ten times as fast in two-thirds dioxane. To compare a completely nonaqueous solvent we studied the reaction with sodium methoxide in methanol and found that chloroform reacted only about one-seventieth as fast as in water. Since the assumptions involved in deriving eq. 3 depended only on the mechanism of the formation of the dihalomethylene and not upon the solvent used, the equation should fit data in solvents other than water so long as no change in reaction mechanism occurs. For this reason we have determined rate constants for the basic hydrolysis of several haloforms (including iodoform, for which we had no data in water) in addition to those studied previously in 66²/₃% dioxane–water and for the basic methanolysis of four haloforms in methanol. Hughes and Peeling have previously found that bromoform is readily alcoholized by mechanisms of a homolytic character, but that these mechanisms can be excluded and, when they are, the reaction with methoxide ions is kinetically second order.[30] In agreement with this observation we found that the second-order rate constants for the reaction of bromoform with methanolic sodium methoxide varied quite widely within a given run and between different runs even when the runs were carried out under "commercial nitrogen." In the presence of 0.26% diphenylamine, however, the rate constants were reproducible and within the experimental error of those obtained with 1.2% diphenylamine, showing that the inhibition was complete. Apparently the tendency for free radical reactions to intervene increases with increasing molecular weight of the haloform and is greater in methanol than in dioxane–water. The methanolysis rate of dibromochloromethane was not slowed by the addition of diphenylamine and neither were the hydrolysis rates of bromoform, dichloroiodomethane or chlorodiiodomethane in 66²/₃% dioxane–water. The hydrolysis of iodoform in dioxane–water, however, was slowed several fold by diphenylamine. The second-order rate constants obtained for the basic decomposition reactions in methanol and dioxane–water are listed in Table IV.

TABLE IV

KINETIC CONSTANTS FOR THE BASIC DECOMPOSITION OF HALOFORMS

Haloform	10^4k, l. mole⁻¹ sec.⁻¹ 35.0°	50.0°	$\Delta H^\ddagger$, kcal./mole	$\Delta S^\ddagger$, e.u.
	In dioxane–water			
$CHCl_2I$	39.9 ± 0.4[a]	293 ± 5[b]	27.1 ± 1.0	18.3 ± 3
$CHClI_2$	180 ± 10[c]	17.7 ± 0.4	29.0 ± 1.2	18.4 ± 4
CHI_3	28.7 ± 3[b,d]	1.55 ± 0.15[b,e]	29.7 ± 1.5	15.6 ± 5
	In anhydrous methyl alcohol			
$CHCl_3$		0.306 ± 0.005		
$CHBrCl_2$		9.25 ± .05		
$CHBr_2Cl$		6.30 ± .08		
$CHBr_3$		2.41 ± .09[b]		

[a] Data from ref. 3. [b] In the presence of diphenylamine. [c] At 67.1°. [d] At 71.3°. [e] Rate constant determined graphically.

In order to test eq. 3 for solvents other than water, some modifications are required, since no kinetic studies of deuterium exchange of haloforms in solvents other than water appear to have been reported. For those haloforms that do not contain fluorine, in water k_2 is so small compared to k_{-1} that the relation

$$k_2/k_{-1} = k_h/k_1 \qquad (5)$$

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(29) (a) H. Böhme, H. Fischer and R. Frank, *Ann.*, **563**, 54 (1949); (b) J. B. Conant, W. R. Kirner and R. E. Hussey, THIS JOURNAL, **47**, 488 (1925); P. D. Bartlett and L. J. Rosen, *ibid.*, **64**, 543 (1942); (c) D. N. Glew and E. A. Moelwyn-Hughes, *Proc. Roy. Soc.* (*London*), **A211**, 254 (1952); (d) B. V. Tronov and E. A. Krüger, *J. Russ. Phys.-Chem. Soc.*, **58**, 1270 (1926); (e) H. J. Backer and W. H. Van Mels, *Rec. trav. chim.*, **49**, 363 (1930); K. A. Cooper, E. D. Hughes, C. K. Ingold and B. J. MacNulty, *J. Chem. Soc.*, 2038 (1948); H. R. McCleary and L. P. Hammett, THIS JOURNAL, **63**, 2254 (1941); G. H. Grant and C. H. Hinshelwood, *J. Chem. Soc.*, 258 (1933); A. Slator, *ibid.*, **85**, 1286 (1904); **87**, 4281 (1905).

(30) Private communication from E. D. Hughes and E. R. A. Peeling quoted by C. K. Ingold, ref. 24, p. 330.

holds very well. For $CHBrCl_2$, $CHBr_2Cl$ and $CHBr_3$ the relation

$$\log \frac{k_1^{CHCl_nBr_{3-n}}}{k_1^{CHCl_3}} = nQ \qquad (6)$$

where Q is a constant (equal to 0.73 at 0°), is a good approximation,[7] assuming that the kinetic isotope effects are the same for all of the haloforms. With the reasonable assumption that these two approximations are also good in methanol and dioxane–water, eq. 5 and 6 may be combined with eq. 3 to give

$$\log \frac{k_h^{CHBr_nCl_{3-n}}}{k_h^{CHCl_3}} =$$

$$\log \frac{n}{3} + n[Q(1 + c - d) + M_{Br}] + (N_{Br} - M_{Br}) \qquad (7)$$

This equation permits the correlation of three data in terms of two parameters. By a least squares treatment the following were calculated as the optimum values for $Q(1 + c - d) + M_{Br}$ and $N_{Br} - M_{Br}$, respectively: for $CHCl_3$, $CHBrCl_2$, $CHBr_2Cl$ and $CHBr_3$ in $66^2/_3\%$ dioxane–water at 35.7°, −0.613 and 2.466; and in methanol at 50°, −0.530 and 2.507; by an analogous treatment for $CHCl_3$, $CHCl_2I$, $CHClI_2$ and CHI_3 in 66 $^2/_3\%$ dioxane–water at 50°, −1.377 and 2.950. These three sets of values permit the calculation of the three relevant rate constants with average deviations of 3, 7 and 16%, respectively. The difference between these values and the analogous ones that may be calculated from the data for pure water are not sufficient to permit any significant conclusions to be drawn.

Experimental

Reagents.—The methods of purification of chloroform, bromodichloromethane, chlorodibromomethane, bromoform, dichloroiodomethane and dioxane have been described previously.[3] Methanol was purified with magnesium by the method described by Fieser.[31] Reagent iodoform and Eastman Kodak Co. white label diphenylamine were used without further purification. Chlorodiiodomethane was prepared by the method of Auger,[32] 158 g. of crude product and 95 g. of twice-fractionated (under nitrogen) material, b.p. 101–102° (33 mm.) being obtained from 312 g. of iodoform and 100 g. of mercuric chloride.

Some of the dichloroiodomethane was prepared by the method of Auger[32] and some was synthesized in the following manner. A solution of 137 g. (0.9 mole) of sodium iodide and 99 g. (0.6 mole) of bromodichloromethane in 250 ml. of methanol was stirred at reflux while 14 g. (0.35 mole) of sodium hydroxide in 35 ml. of water was added dropwise over a period of 30 minutes. After 15 additional minutes of refluxing, the material was allowed to cool overnight and then water was added, causing separation into two layers. The organic layer was taken up in methylene chloride and combined with a hexane extract of the aqueous layer. After the methylene chloride and hexane had been removed by distillation through a 30-inch column at atmospheric pressure, the pressure was reduced to 110 mm., where 61 g. of dichloroiodomethane (n^{23}_D 1.5810) was collected between 73 and 74°. In addition to the 49% yield in this main fraction 8% was obtained in fore- and after-runs within 5° of it.

"Oxygen-free" water was prepared by boiling distilled water and cooling it under nitrogen or by bubbling nitrogen through the water for a prolonged period. Carbonate-free sodium hydroxide was made by dilution of a filtered ~20 M solution.

Kinetic Runs.—Our temperature-control methods have been described previously.[3] Kinetic runs were carried out by several different methods. In method A a known volume of a standard solution of haloform in the appropriate solvent or solvent-mixture was thermostated in a volumetric flask, and at zero time a thermostated standard solution of base was pipeted into the flask. In the cases of most reactions at 50° and above, and those reactions at 20° and above that required several days to run, samples were pipeted from the reaction flask into a flask containing some clean ice, and the unreacted base was titrated with standard acid (either hydrochloric or perchloric). For purely aqueous or aqueous dioxane solutions phenolphthalein was used as the indicator. In methanolic solutions either *p*-nitrophenol or curcumin (turmeric yellow) was used. In other reactions the reaction sample was pipeted into a known volume (excess) of standard acid and the excess acid back-titrated. All operations except the final titration were carried out under nitrogen. Method B was a modification of A in which a small volume of ~5 N sodium hydroxide solution was added by syringe at zero time. The initial base concentration was calculated by extrapolation from several points taken as soon as possible. Method C resembled A except that a number of flasks containing standard haloform solutions were made up and a known volume of base added to each at zero time. To take a point, the entire contents of a flask were poured onto ice or into an excess of acid and the flask was rinsed twice with distilled water. In runs where diphenylamine was used, it was weighed out with the haloform.

Method A was used for studying the hydrolysis of dibromochloromethane at 0° and of bromodichloromethane at 35° in aqueous solution. Method C was used for the hydrolysis of chloroform in water, dichloroiodomethane in aqueous dioxane and in water at 35°, and iodoform in aqueous dioxane. Method B was used for all of the other reactions except those on which the data are quoted from other articles.[6-8]

Calculations.—Rate constants were calculated by use of the second-order rate equation employed previously

$$kt = \frac{2.303}{(3 + f)a - b} \log \frac{a(b - x)}{b(a - [3 + f]x)} \qquad (8)$$

where $a = [CHX_3]_0$, $b = [OH^-]_0$ or $[OMe^-]_0$, $x = \Delta[CHX_3]_t$, t = time (sec.), and $3 + f$ is the number of moles of base that react per mole of haloform, f being the fraction of haloform that produces formate in cases where carbon monoxide and formate ions are the only products. Although it is difficult to determine f very accurately, fortunately, the value of k obtained is rather insensitive to the value of f used in the calculation. Since the values of f obtained for chloroform at various temperatures in water and aqueous dioxane did not vary beyond the rather considerable experimental error (in determinations in which the halide and hydroxide ion concentrations were measured) we used the value 0.15, obtained previously,[14] in all calculations on chloroform in water-containing solvents. Since the value of f should depend only on the nature of the dihalomethylene intermediate, the value 0.15 also was used for bromodichloromethane and dichloroiodomethane whose hydrolysis, like that of chloroform, proceeds through dichloromethylene as an intermediate. For bromoform and dibromochloromethane in aqueous solvents a value of 0.08 was used, since a number of determinations showed this value to be very probably within a factor of two of the correct value. For all of the runs in methanol and for iodoform and chlorodiiodomethane in aqueous solvents, a value of zero was used for f since the values obtained experimentally were quite low (sometimes negative) and poorly reproducible.

In some cases the rate constants calculated from eq. 8 fell (never so much as 20%) as the reaction proceeded. In these instances (noted in Tables I and III), which may have been due to the presence of such reactive impurities as carbonyl halides, the rate constants were determined from the slope of plots of the right-hand side of eq. 8 *vs.* t.

Heats and entropies of activation listed were calculated from the absolute rate equation[33]

$$k = \frac{\mathbf{k}T}{h} e^{-\Delta H^\ddagger/RT} e^{\Delta S^\ddagger/R}$$

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[31] L. F. Fieser, "Experiments in Organic Chemistry," 3rd ed., D. C. Heath and Co., Boston, Mass., p. 289.

[32] V. Auger, *Compt. rend.*, **146**, 1037 (1908).

[33] S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y. 1941, p. 14.

Jr., Mr. Billy D. Oakes, Mr. Paul B. Langford and Mr. Franklin P. Prosser, each of whom determined one or two of the rate constants reported herein; to the Rich Electronic Computer Center for use of their equipment; and to Dr. Bertram M. Drucker for instruction in computer techniques.

ATLANTA, GEORGIA

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Lead Tetraethyl as Initiator for Polymerization Reactions[1]

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Polymerizations of acrylonitrile have been accomplished with lead tetraethyl and lead tetraethyl–titanium tetrachloride catalysts. The latter catalyst was found to be effective in certain cases where the former was not. The presence of light, especially ultraviolet light, was found to be not only very beneficial but a necessity in reactions at low temperatures (around room temperature). The polymers produced had inherent viscosities in the range 0.9–5.0, but possessed none of the highly crystalline properties of olefin polymers prepared using the normal Ziegler catalysts.

Polymerizations using Ziegler catalysts have so far been restricted to α-olefins. Monomers containing functional groups (*e.g.*, vinyl chloride, acrylonitrile, etc.) appear to react with the usual catalysts, such as an aluminum trialkyl–titanium tetrachloride mixture, and destroy them. In an effort to find different catalysts which these monomers would not attack, it was thought that the heavier, less reactive metal alkyls might be of more use. Because of its ready availability, lead tetraethyl was among those metal alkyls studied.

A recent patent application[2] describes the use of a lead tetraethyl–titanium tetrachloride catalyst in the polymerization of olefins to yield highly crystalline polymers. These reactions usually were carried out under pressure with reaction temperatures of 90–180°.

The monomers selected for the present work were vinyl acetate, vinyl chloride, acrylonitrile and methyl methacrylate. A catalyst of lead tetraethyl and titanium tetrachloride was prepared in dry heptane and the reaction temperatures ranged from 0–60°. The best results were obtained with acrylonitrile and methyl methacrylate and, due to their similarity of reaction, a thorough investigation was undertaken with acrylonitrile. Typical results with this monomer are listed in Table I.

TABLE I

POLYMERIZATION OF ACRYLONITRILE USING LEAD TETRAETHYL-TITANIUM TETRACHLORIDE AS CATALYST

Lead tetraethyl, % (based on monomer)	Titanium tetrachloride/lead tetraethyl (molar ratio)	Temp., °C.	Time, hr.	Conversion, %	Inherent viscosity in dimethylformamide, 25°
3.6	0.78	25	72	8.8	2.4
3.6	.78	50	48	23	4.5
3.6	.78	60	72	17	2.4
3.6	1.56	60	72	13	2.4
3.6	3.90	60	72	5.1	0.9
7.2	0.36	60	72	4.8	1.8
18.0	0.16	60	72	3.7	2.0

A few reactions were run in duplicate and it was found that yields could be checked to ±0.5% and viscosities fell in the same general range.

These results indicated that a large excess of either catalyst component was undesirable as both the conversion and inherent viscosity were lowered. While reaction would go at room temperature, heating at 50° seemed to give the best results. Increasing the temperature did increase the conversion, but lowered the viscosity of the product. Control reactions were run using lead tetraethyl alone and titanium tetrachloride alone as catalysts at 50° for 48 hours. No polymer was obtained from the titanium tetrachloride reaction but an 8% conversion was obtained using lead tetraethyl. This polymer had an inherent viscosity of 5.0.

X-Ray diffraction pictures of the polyacrylonitrile samples prepared from lead tetraethyl alone and from lead tetraethyl–titanium tetrachloride showed that neither polymer had highly crystalline properties. Further work involving changes in catalyst ratios and changes of solvent failed to produce any better results. Prolonged reaction times would raise the conversion but not sufficiently to be of great use.

Attention was then shifted to experiments involving the use of lead tetraethyl alone as catalyst. Numerous examples of free radical polymerizations involving lead tetraethyl as a catalyst can be found in the literature. However, they usually involve reaction temperatures in the range 200–400°, and often the polymerizations are run under high pressure. Young and Douglas[3] used lead tetraethyl as a catalyst in the polymerization of vinyl acetate and vinyl chloride in acetone solution. These reactions were run in an autoclave at 80–100°. No mention of the use of acrylonitrile was made.

Polymerizations of acrylonitrile using a lead tetraethyl catalyst went smoothly, although high conversions were not obtained. In an effort to increase the conversions, the use of ultraviolet light on the reactions was tested and found to be of great benefit. Higher conversions were obtained although smaller inherent viscosities indicated that lower molecular weight polymers were obtained.

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(1) The work discussed herein was partially supported by a grant from the National Science Foundation for polymer research.

(2) Montecatini, Societa Generale per l'Industria Mineraria e Chimica, Australian Patent Application 26-356-16995, March 23, 1956.

(3) C. O. Young and S. D. Douglas, U. S. Patent 1,775,882, September 16, 1930.